Indian J Phys. **71A** (4), 443–451 (1997)

IJP A
— an international journal

Open circuit thermally stimulated currents in polyvinyl pyrrolidone films

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Received 15 May 1996, accepted 27 December 1996

Abstract : Study of open-circuit thermally stimulated currents (TSCs) has been made on 50 μm thick, one-sided vacuum aluminized polyvinyl pyrrolidone samples The samples were thermally poled under different field and temperature conditions, varying from 10-100 kV/cm and 50-130°C, respectively. The polarity of the current at low temperature side during heating, corresponded opposite to that of the charging current For samples poled under low values of field and temperature on high temperature side, the current was observed to be of the same polarity as that of the charging current Such currents were characterized with two peaks of opposite polarity TSCs of the sample poled under relatively higher field and temperature condition were of the same polarity as that of the charging current over the whole temperature range during heating. Such TSCs usually well characterized with two peaks located around 80–95°C and 150–170°C, respectively The high temperature peak has been observed to shift towards lower temperature with increase in poling field values

Keywords : Open circuit TSC, polyvinyl pyrrolidone, dipolar polarization

PACS Nos. : 72 20 Jv, 73 99 +f

1. Introduction

Information on the charge storage and transport phenomena in polymer electret is of great interest for several industrial applications [1,2]. The thermally stimulated current (TSC) is a useful and popular technique, for understanding charge storage and charge decay processes in electret. The TSC method consists of (a) polarization of the specimen under the specified conditions of electric field and temperature for a stipulated period and (b) the poled sample, *i.e.*, thermoelectret, is afterwords depolarized through a current recording device under

thermal stimulation, *i.e.* heating the electret with a constant rate. The charge decay processes are thus, investigated as a function of temperature instead of time. Charge decay measurements at room temperature are rather time consuming as dipoles and space charges virtually remain immobile. Thermal stimulation results in quick regaining of freedom of motion Thus, thermal stimulation of discharge reduces the measurement time considerably Various reports on thermally stimulated current (TSC) behaviour of polyvinyl pyrrolidone [3–6] and different relaxation processes contributing to the observed peaks in the corresponding thermograms are available. However, the role of various polarization processes and their relative contribution to the electret state of the polymer is not yet fully understood. Charge storage may be due to either dipolar orientation or space charge To study the decay of one sided metallized homoelectret, Turnhout and coworkers [1,2] modified Frie and Groenitzer method [7] by introducing an air gap between non-metallic side of specimen and adjacent metal electrode. When such a two layer assembly is heated, a displacement current is generated by image charges released from the non-contacting electrode as the air gap prevents the electret charges from recombining with the image charges of the upper electrode. Since the electret itself is not shorted, the electric field within the electret is no longer zero and in fact, becomes quite large. Consequently, the ohmic conduction current flowing through the electret, produces an appreciable external displacement current, whereas it remains occurred in thermally stimulated discharge current (TSDC) of shorted electret. In short circuit TSC of homogenous electrets, the neutralization of space charges by ohmic conduction is not observed which can however, be observed in open circuit TSC In open circuit TSC, there exists a net field which causes the space charges to be neutralized by net unidirectional ohmic conduction current that is externally observable. This utilization gives rise to current peak that can be expected to resemble the space charge peak. Open circuit TSC also enables one to decide whether the electret contains a homocharge or a heterocharge or both. The open circuit thermally stimulated current (TSC) study reveals the transport rate (mobility) of charges and thus, is valuable in predicting the lifetime of an electret [8]. The present study has been undertaken in polyvinyl pyrrolidone (PVP) with the view to obtaining a better insight into the mechanisms responsible for charge storage and release in this polymer.

2. Experimental details

Polyvinyl pyrrolidone (PVP) is a growing polymer in the field of pharmaceutical sciences [9] because of its ability to form complexes with various drugs. In PVP, the asymmetric monomers are present in the structure and possesses a side group (as pyrrolidone ring) PVP is known as a polar polymer, due to its carbonyl group of double bond in pyrrolidone ring [10]. The network structure of PVP has different lengths of π and σ bonds in between nitrogen, oxygen, carbon and hydrogen atoms [11,12].

The solution was prepared in a glass beaker by dissolving 2.4 gm PVP in 30 ml of chloroform at room temperature. The solution was continuously stirred for about 30 minutes by means of a teflon-coated magnetic stirrer. Thereafter, the solution was stirred

and heated to 50°C to ensure a homogeneous mixing of solvent. The glass beaker containing the solution was then immersed in a constant temperature oil bath. Ultrasonically cleaned glass slides were immersed vertically into the solution for a period of 20 minutes. After the film deposition, the glass slide was taken out and outgassed in air at 50°C for 24 h, followed by room temperature outgassing at 10^{-5} torr for a further period of 24 h. Vacuum coated electrodes were used throughout the work. The thickness of the sample was approximately 50 μm. The geometry of the sandwich configuration of the electrodes and thickness of the sample was same as reported earlier [13,14]. A schematic diagram showing the sample mounting in open circuit condition [15] is shown in Figure 1. The sample polarization and current TSD measurements in open circuit configuration have been carried

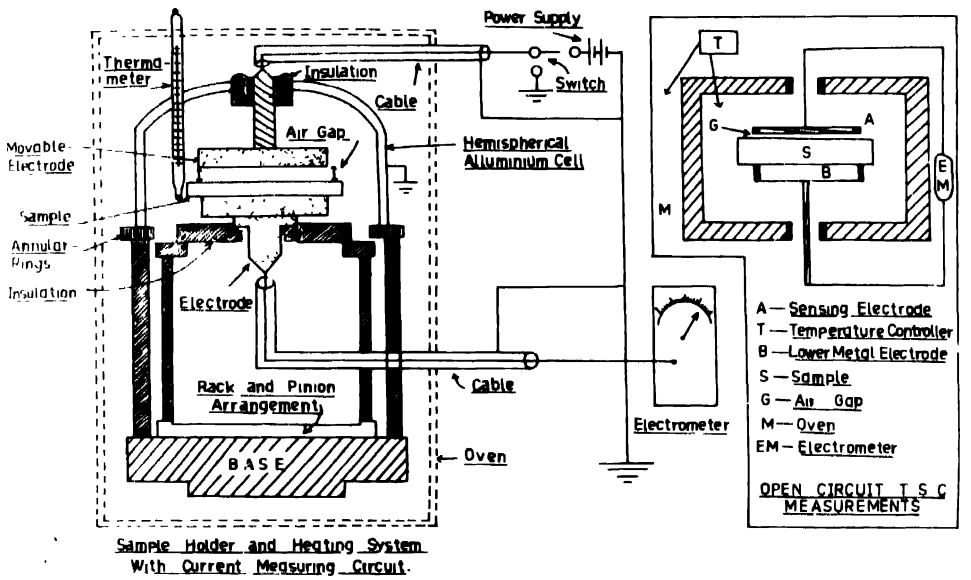

Figure 1. Sample mounting in open circuit condition

out in a suitable cell using an assembly which is dry, rigid and well-established. This assembly have the following properties-(i) high insulating resistance, (ii) freedom from picking up of spurious potentials and induced charges due to physical motion of the system, iii) negligible leakage current and less microphonic. To achieve the required degree of precision every consideration of perturbing parameters was taken into account, while designing the electrode assembly.

The samples were thermally polarized with fields E_p of 10, 20, 30, 50, 75 and 100 kV/cm at temperatures T_p of 50, 70, 90, 110 and 130°C. After polarizing for 1 h at the desired temperatures, the samples were cooled to room temperature under the application of the field. Total time of polarization was adjusted to be 2 h in each case. The polarized samples were subsequently short circuited for an arbitrary time of 10 minutes for excluding

the confusing contribution of unstable charges which stay on the electret surface after charging.

For registering TSC in open circuit, the polarized samples were mounted in an electrode assembly with the non-metallic surface parallel to the sensing electrode (metal electrode of the assembly) at a distance of 3 mm, while the metallized surface rested on the other metal electrode. The sensing electrode was connected to the electrometer. A high voltage power supply, EC-4800 D, provided stabilized DC voltages for polarization. The observed low level current were measured using high precision electrometer amplifier (Keithley 600 C). The electrometer is specially designed to measure very small *direct current*, low DC potentials from high impedence source, small charges and high resistance. The requirement of additional filters for noise elimination is not required.

3. Results and discussion

The characteristic open circuit thermally stimulated current curves for the thermo electrets poled with various fields (10, 20, 30, 50, 75 and 100 kV/cm) at a fixed temperature T_p (= 70°C) and at different temperatures (50, 70, 90, 110 and 130°C) with a fixed field (= 40 kV/cm) are shown in Figures 2 and 3 respectively. It is observed that for samples poled with comparatively lower field (*i.e.* 20, 30 and 50 kV/cm) the current is negative

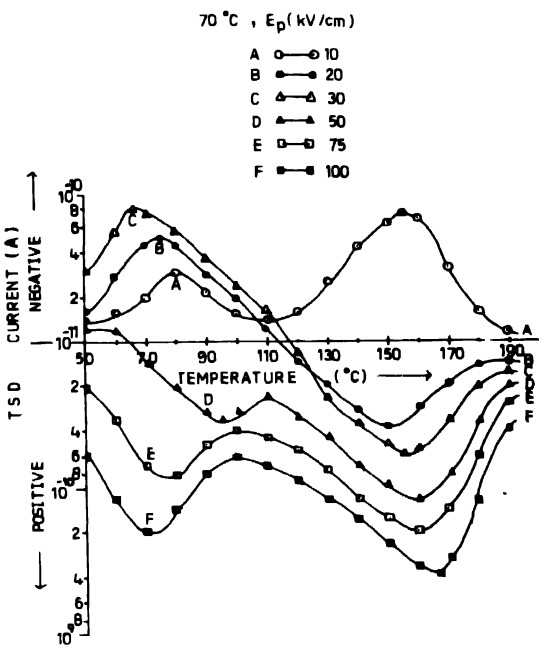

Figure 2. Open-circuit TSC spectra for polyvinyl pyrrolidone samples poled with different fields (10, 20, 30, 50, 75 and 100 kV/cm) at 70°C

initially and becomes positive at higher temperature during heating. However, for lowest poling field (*i.e.* 10 kV/cm) the current has been observed to be negative throughout the heating span and characterized with two peaks at 80 and 155°C, respectively. The samples poled with the fields 20 and 30 kV/cm are characterized with two peaks around 75–80°C and 150–155°C, respectively and in a direction opposite to each other. The currents for

samples poled with higher values of field (*i.e.* 75 and 100 kV/cm) have been observed to be positive (*i e.* of the same polarity as that of the charging current) over the whole heating span These currents have been found to be characterized with two well defined peaks; one located between 70–80°C and the other between 160–170°C Generally, the high temperature peak has been found to shift towards higher temperature side with increase in poling field value.

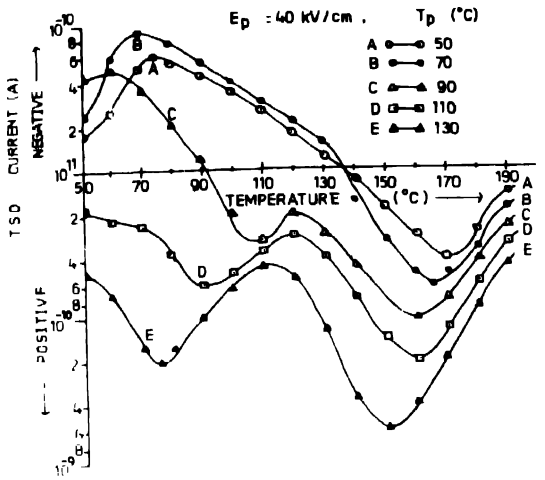

Figure 3 Open circuit TSC spectra for polyvinyl pyrrolidone samples poled with 40 kV/cm at different poling temperatures (50, 70, 90, 110 and 130°C)

Similar nature of the curves has been observed for samples poled at different polarizing temperatures (Figure 3). For the three values of poling temperatures (*i e.* 50, 70 and 90°C) two peaks in negative and positive direction respectively, have been observed However, for the higher polarizing temperatures (*i.e* 110° and 130°C), no change of sign of polarity of currents has been observed. Generally, the low and high temperature peaks have been found to shift towards lower temperature side with increase in polarizing temperature

The activation energy value of low-temperature peak which is located between 60–90°C, has been found to vary from 0.28 to 0.35 eV. However, this value for high-temperature peak located between 150–170°C, has been found to be 0.47 to 0.88 eV.

In the case of open-circuit TSC, the charge carriers injected from outside and trapped near the non-metallic surface of the electret, will not be able to recombine with the image charges at the adjoining electrode due to blocking by adjacent air gap This blocking will cause these carriers to move towards the other electrode through the bulk of the sample. Thus, these carriers will fill the sample uniformly. This will give the unidirectional motion to these carriers. The motion of these carriers towards the lower electrode will release the charge carriers induced on the coated electrode, which will generate the current of the polarity similar to that of the charging current.

Thermal polarization of the sample may be due to various mechanisms, (i) dipole relaxation polarization, (ii) displacement of charge carriers within molecular or domain

structure throughout the solid, (iii) relaxation polarization of Maxwell-Wagner type caused by micro- or macro-heterogenities of continuous or discrete nature, (iv) charge injection from electrodes with their subsequent trapping in traps, (v) electrode polarization due to complete or partial electrode blocking and (vi) tunnelling of charge from the electrodes to empty traps. The first three mechanisms result into the formation of heterocharge, the polarity of which is opposite to that of the charging electrode. However, the remaining three mechanisms give rise to formation of homocharge. The decay of net charge of an electret during TSC results from dipole reorientation, space charge motion and ohmic conduction. So far as, the dipole disorientation will flow in a direction opposite to that of charging current whether the electret is shorted or blocked by an air gap during heating. Thus, it is clear that the dipole disorientation in the present case will generate TSC of negative polarity. The space charges due to charge carriers generated in the bulk of the sample during formation will be utilized by recombining with the charge of opposite sign. This will also generate TSC of negative polarity. However, if the space charges are formed due to injected charges then such charges will be neutralized at the electrodes during formation. Hence, such space charges will give rise to the TSC of the polarity as that of the charging current *i.e.* the TSC will be of positive sign. During open circuit TSC experiment, the decay of heterocharge is supposed to produce TSC of polarity opposite to that of charging current, which in the present case should be negative, while, the decay of homocharge should produce TSC of the polarity of charging current *i.e.* positive current. In the present case, open circuit TSCs of positive polarity have been observed for the samples poled with higher values of fields and are characterized with two peaks. However, for samples poled with lower values of fields, the current has been found to be negative at lower temperatures, which then reverses and becomes positive at higher temperatures during heating. We know that for most polymers (which is true for PVP also), a distributed polarization is more likely. In such case, if the electret is formed at low temperature and field, then its polarization is likely to be incomplete. The group of dipoles with small relaxation time are likely to orient during formation while the dipoles with high relaxation time may not respond during the charging process. In this situation, the electret will give rise to the first peak of negative polarity originating from the disorientation of the dipoles of low relaxation frequency. The second peak on the high temperature side should be of positive polarity due to the orientation of dipoles with high relaxation frequency. It is also suggestive that in the first instance, homocharge formation in the samples due to one or more of the last three mechanisms mentioned above, is stronger than the heterocharge formation.

The observation of low-temperature peak with negative current for samples poled with lower values of fields and with positive current for samples poled with higher values of field, indicates that the peak is contributed by dipole orientation as well as by space charge polarization. The classical theory [16,17] for the decay of charge of an electret assumes the superposition of homocharge and heterocharge. The increasing value of current at low-temperature peak and the observed activation energy values indicate that the peak

may be contributed significantly by dipolar and ionic polarizations. Polyvinyl pyrrolidone is known as a polar polymer due to its carbonyl group of double bond in pyrrolidone ring [10]. The carbonyl group of PVP may possess orientation with respect to the active groups [18]. TSC thermograms for PVP samples are characterized with two major peaks in the ascending order of temperature and designated as α and ρ-peak respectively. The α-peak is a dipolar peak and may be attributed to disorientation of polar side group. The ρ-peak is associated with the primary relaxation process which occurred in the temperature range of rubber glass-transition of PVP (around 150–170°C). The value of E associated with this peak suggest the possibility of ionic processes. PVP exhibit the properties of solid free radical, probably at the temperature of phase transition; hence, the ionic and other electronic charges may certainly be present during the polarization of the sample associated with ρ-peak. This agrees with the earlier findings [4–6]. This group is attached to the main chain with an amide bond. The shifting of lower side peak over a particular temperature range, the observed difference in activation energy values indicates that at lower fields, the polarization is not saturated and increasing value of polarizing fields lead to the completion of dipolar polarization. A more complex behaviour is obtained from the processes involving space charge polarization, since generally the build-up, release and equilibrium spatial distribution of the charge are strongly-dependent on the applied field. When transitional or space-charge polarization due to microscope charge transferred towards the electrodes with subsequent trapping occurs, a field dependent peak position and a more or less complicated non ohmic behaviour is observed.

In the case of sample poled with 10 kV/cm, both the observed peaks are of negative polarity. This indicates that the corresponding electret is strongly heterocharge electret. The heterocharge formation may be due to different groups of dipoles with different relaxation times will disorient at low temperature giving rise to low temperature peak of negative polarity while the oriented dipoles with high relaxation time will disorient at high temperature giving rise to high temperature peak of same polarity *i.e.* of negative polarity. Thus, the whole thermogram may be of negative polarity. The observed thermograms characterized by both the peaks of positive polarity show that the corresponding thermoelectrets are strongly homocharge electrets. For highly heterocharge electrets, the heterocharge will decrease in the beginning and will give rise to heteropolar discharge current of negative polarity. However, at high temperatures, when the conduction arises sharply, a homocharge is expected to build up and the TSC is expected to reverse sign from negative to positive. Thus in such cases, the low temperature peak of positive polarity is expected. In practice, however, ohmic conduction becomes operative latter than the dipole reorientation. Hence, the current of positive polarity will hardly be observable when any homocharge is lacking initially. The ohmic conduction emerges when most dipoles are reoriented, so that internal field is too small to create an appreciable homocharge. Thus, in practice, a current of positive polarity in high temperature region is found which is likely to arise from a true homocharge.

Considering the origin of the high temperature to be mainly due to space charge polarization, the thermograms show that the traps are distributed spatially as well as energetically. The occurrence of well-defined and non-overlapping peaks, indicates that the polymer contains trapping levels of at least two different depths with certain narrow energy distribution. The current measured in open circuit configuration has been found to be highly sensitive to the trap structure of the material. The microscopic transport of charge carriers giving rise to TSCs can be described in terms of Mott-Davis Model, which distinguishes between transport over (i) extended states, (ii) band tail states (localized), and (iii) states near the Fermi level (localized). The detailed nature of the observed thermograms seems to be in accordance with the description of charge trapping and transport suggested by this model. The observed activation energies for high temperature peak are in the range of 0.47 to 0.86 eV derived out of the experimentally observed thermograms, allowing however, no conclusions about the fast transport porperties.

During charging, the traps are always successively filled, beginning with the deepest sites. Thus, upon heating the charged sample, the carriers in the shallowest level, become mobile with free path much shorter than the sample thickness. The effective velocity of the charges is slowed down due to the presence of traps in the material. With the rising temperature, the measured current increases due to the increase in number of available carriers in quasi-conduction band. This explains the initial exponential increase in current. The current appears maximum, because the free carriers (in quasi-conduction band) are captured in deeper traps, with longer release time and become immobile. Upon further heating, however, the carriers in the next deeper trap become mobile and the process repeats giving rise to other peak in the thermograms as observed in the present case.

The systematic analysis of various results have indicated that the polarization phenomena in the present case is the combination of dipole orientation as well as the trapping of charge carriers leading to the formation of space charge.

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